

NISTIR 6527

Measurement Needs for Fire Safety: Proceedings of an International Workshop

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In-Situ Gas Concentration Measurements for Fires

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Definition of *In-Situ*

- Not intrusive
- Does not alter environment
- Involves lasers and detectors
- Employs spectroscopy

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Selecting a Method

- Consider application: bench scale experiment, product test, reduced scale enclosure, full scale burns
- What are you measuring? How much is there? What is the temperature?
- What other things are there? gases, early soot, mature soot, droplets
 - these could be interferences
 - also could attenuate or steer light
- Optical Access Possibilities
- \$\$\$\$\$ Budget Time Budget
- Available Expertise? technician, engineer, trained MS or PhD laser diagnostician
- Many applications require two or more methods

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Comments on Accuracy

- Major uncertainty sources are systematic errors associated with converting a measured quantity into a concentration
 - temperature effects
 - collisional environment
 - laser power fluctuation, laser line center/shape drift
 - soot extinction, beam steering/defocusing
- Accuracy sometimes expressed as “detection limit”



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Spontaneous Raman Scattering

- Used for Major Species Concentrations
 - H_2 , N_2 , O_2 , CH_4 , CO_2 , CO
- Inelastic scattering of laser light by molecules
 - Incoherent (scatters in every direction)
 - No specific λ_{laser} is required, although lower $\lambda_{laser} \Rightarrow$ higher signal
 - Scattering at $\lambda_{emission} > \lambda_{laser}$ (Stokes) and $\lambda_{emission} < \lambda_{laser}$ (Anti-Stokes)
 - Several molecules detectable by monitoring several $\lambda_{emission}$ simultaneously
 - Suffers interference from PAH LIF, Other Raman, Rayleigh
 - Can suffer interference from wall & particulate scattering
 - **Weak Signals**
- Temporal resolution \Rightarrow (typ. $< 1 \mu s$) \Rightarrow determined by detector gate or laser
- Spatial resolution \Rightarrow (typ. $< 1 mm^3$) \Rightarrow determined by collection optics
- Often Combined with Rayleigh Scattering for Temperature & Concentration

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Rayleigh Scattering

- Signal proportional to total ρ -- all molecules contribute
- Used primarily for Temperature
- Can be used for gas concentration in isothermal binary mixtures
- Elastic scattering of laser light by molecules ($\lambda_{emission} = \lambda_{laser}$)
 - Incoherent (scatters in every direction)
 - Requires clean environment
 - Signal much stronger than Raman Scattering
- Temporal resolution \Rightarrow (typ. $< 1 \mu s$) \Rightarrow determined by detector gate or laser
- Spatial resolution \Rightarrow (typ. $< 1 mm^3$) \Rightarrow determined by collection optics
- Can suffer interference from wall & particulate scattering

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Laser Induced Fluorescence (LIF)

- Used for Minor Species Concentrations
 - OH, CH, NO, CO routinely probed
 - Also possible to probe H₂, O₂, H₂O, O, H & other atoms
 - Mixing tracers such as added acetone
- Laser light => photon absorbed by molecule => light emitted
 - A molecule can have several $\lambda_{\text{emission}}$ (same & different from λ_{laser})
 - Incoherent (emitted in all directions)
 - Orders of magnitude stronger signals than Raman scattering
 - Sensitive to quenching
- Temporal resolution => (typical < 1 μs) => determined by detector gate or fluorescence lifetime
- Spatial resolution => (typical < 1 mm³) => determined by collection optics
- Can suffer interference from PAH LIF, Rayleigh
- Can suffer interference from wall & particulate scattering

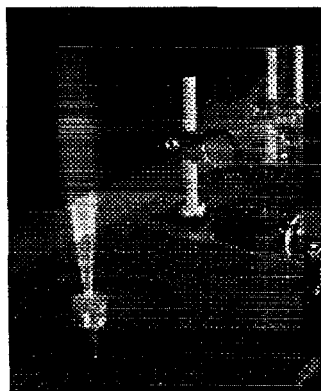
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Planar Imaging Measurements

- CH, C₂, CN, NO, H, O, CO,
Tracers (acetone)
- Mostly qualitative
- Planar Rayleigh, Planar LIF (PLIF)
- Can be performed simultaneously
with planar velocimetry
- Suffer from Raman, Rayleigh, LIF
interference sources
- PLIF requires intensified CCD
cameras



SNL Website

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Coherent Anti-Stokes Raman Scattering (CARS)

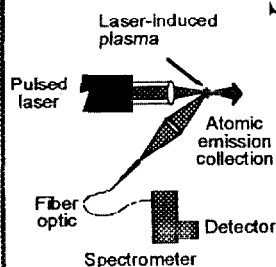
- Used for Major Species N_2 , O_2 , CO , H_2 , H_2O concentrations $> 1\%$ vol
- 2 or 3 incident laser beams with special λ_{laser}
 - Produce a coherent (directional) signal beam with an additional λ
 - Can be used in mildly sooting environments
 - Multiple species and/or temperature
 - Signal orders of magnitude stronger than spontaneous Raman
 - Complicated spectra/signal processing
 - Suffers from non-resonant spectral background interference
- Spatial Resolution: Defined by laser overlap geometry (typical $\sim 1 \text{ mm}^2$)
- Temporal Resolution: (typical $< 1 \mu s$) defined by detector gate or laser pulse
- Accuracy: detection limit $\sim 1\%$

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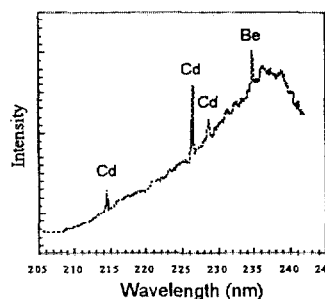


Laser Induced Breakdown Spectroscopy (LIBS)



- Uses spectral information to measure multiple metals
- Good for inorganic species
- Temporal resolution \propto plasma lifetime $\approx 100 \mu s$
- Spatial resolution $\approx 2 \text{ mm}$
- Detection limits $O(\text{ppb})$

- * Line position provides species identification
- * Line intensity provides species concentration



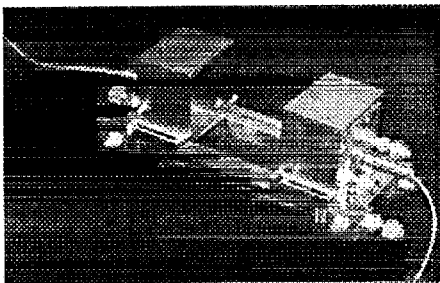
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Tunable Diode Laser Absorption (TDLAS)



- fiber optics
- low-cost miniature lasers
- water-cooled
- purged optics
- quantifiable spatial & temporal resolution
- quantifiable uncertainty
- fast measurements
- use in sooty environments
- detect multiple species simultaneously

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Laser Absorption Spectroscopy

- Laser photon absorbed by molecule
 - traditionally performed using lamps
 - path-averaged measurement
 - now performed with tunable diode lasers
- Near-infrared communication lasers: spectrally narrow
 - H_2O , T, soot, CO, O_2 , CO_2 , CH_4 , C_2H_2 , C_2H_4
also HCN, HCl, NO, NO_2 , OH, H_2S , NH_3
- Lasers \Rightarrow narrow spectral coverage
 - $\sim 2.5 \text{ nm}$ (10 cm^{-1}) for temperature-tuning
 - $\sim 0.5 \text{ nm}$ (2 cm^{-1}) for current-tuning

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TDLAS Challenges

- Weak overtone molecular transitions
 - Need to measure $\tau \sim 0.99999$
- Line shapes change with T & collision partners
- Congested spectra
 - H_2O primary culprit
 - Hot bands at high temperatures
 - Unknown high-temperature spectroscopy
- Interferometric noise (etalons)
- Beam steering/optical alignment

– Spatial Res.: Can be ~ 10 cm
 – Temporal Res.: Can be < 1 ms
 – Accuracy:
 • τ of 0.99999 or 0.9999 achievable
 • space/time/T *trade-off*
 • CO \Rightarrow 0.1% per m, 200 ms, 300 K

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Year 2000 TDLAS Work Fires and Sooty Flames

- NIST
 - CO, $C_2H_2 \Rightarrow$ quantifying signals & determining uncertainty
- Army Research Laboratory (ARL)
 - HF, O_2 , hydrocarbons \Rightarrow suppressant effectiveness, fuel-to-air ratio
- Sandia National Laboratories (SNL)
 - H_2O , soot, temperature, C_2H_2 , $CO_2 \Rightarrow$ real-scale fire hardware
- Naval Research Laboratory (NRL)
 - O_2 for large-scale suppression studies
- Stanford/Navy Pulse Detonation Engines
 - T, soot fraction, 2-color soot absorption/emission, multiplexed diodes

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Near-IR TDLAS Success Stories

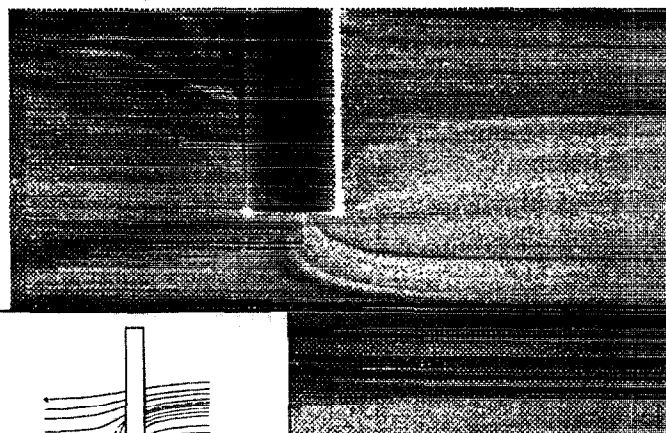
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- Hygrometer flown on wing of NASA P3B research aircraft--Applied Physics B. 67:275 Sonnenfroh et al., 1998
- O₂, CO, and HCl in stack of a 27-MW paper mill boiler/incinerator, HF in aluminum smelter, NH₃ in 460-MW coal boiler flue, Linnerud, et al., Appl. Phys. B 67:297, 1998
- H₂O & T in NASA microgravity drop tower flames--Silver et al., Appl. Opt. 34:2787
- CH₄ sensor in landfill--Hovde et al., J. Atm. Chem. 20:141, 1995

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PIV Study of Extractive Probes



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Summary

	Spatial Resolution	Temporal Resolution	Accuracy (?)	Comments
Raman Scattering	~ 1 mm	< 1 μ s	5 %	Weak Signals Multiple Species
Rayleigh Scattering	~ 1 mm	< 1 μ s	5 %	Clean Environment
LIF	~ 1 mm	< 1 μ s	5 %	Quenching Important
CARS	~ 2 mm	< 1 μ s	5 %	Mild Soot OK Complex Data Reduction
LIBS	~ 2 mm	~100 μ s	5 %	Metals/Toxicity
TDLAS	~10 cm	~1 ms	5 %	Space/Time/Temperature Trade-Off Fire Research Activity

*Accuracy depends on species being measured and its environment, i.e., line strength, temperature dependence of spectroscopy, interfering species, averaging time, beam attenuation and steering, dynamic range of detector, etc.

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Reading List I

- **Laser Diagnostics for Studies of Turbulent Combustion.** E.P. Hassel and S. Linow. *Meas. Sci. Technol.* 11:R37. 2000.
- **Laser Spectroscopic Techniques for Combustion Diagnostics.** Marcus Alden. *Combust. Sci. Tech.* 149:1. 1999.
- **Laser and Probe Diagnostics in Fundamental Combustion Research.** Katharina Kohse-Hoinghaus. *Israel Journal of Chemistry.* 39:25. 1999.
- **Diode Laser Absorption Sensors for Gas-Dynamic and Combustion Flows.** Mark Allen. *Meas. Sci. Technol.* 9:545. 1998.
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- **Laser Induced Fluorescence Spectroscopy in Flames.** John Daily. *Prog. Energy Comb. Sci.* 23:133. 1997.
- **Application of Tunable Excimer Lasers to Combustion Diagnostics: A Review.** E.W. Rothe and P. Andresen. *Applied Optics.* 36:3971. 1997.

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- **The Structure of Nonpremixed Flames Revealed by Raman-Rayleigh-LIF Measurements.** A.R. Masri, R.W. Dibble, and R.S. Barlow. *Prog. Energy Comb. Sci.* 22:307. 1996.
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- **Laser Diagnostics Applied to Combustion Systems.** S.S. Penner, C.P. Wang, and M.Y. Bahadori. *20th Combustion Symposium*. p. 1149. 1984.
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- **Raman Scattering Studies of Combustion.** Marshall Lapp & Danny Hartley. *Combust. Sci. and Technol.* 13:199. 1976.
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